WILLIAM MARSH RICE UNIVERSITY

HOUSTON, TEXAS

Semiannual Status Report #10

On

NASA RESEARCH GRANT NO. NsG-6-59

Covering

Research on the Physics of Solid Materials

For the Period

November 1, 1963 through April 30, 1964

Under the Direction

Of

Franz R. Brotzen

This grant has been in effect for five years. The objective of this grant can be summarized as follows: The performance of fundamental research on the behavior and properties of solid materials and the simultaneous promotion of graduate education of scientists and engineers in this field. This objective has been pursued at Rice with considerable success, as evidenced by the achievements during the six months covered by this report.

At present there are 35 different research projects supported by this grant. These projects are carried out under the direction of 18 faculty members in 6 different departments of the University - Chemical Engineering, Chemistry, Electrical Engineering, Geology, Mechanical Engineering and Physics.

Dr. H. Deans of the Chemical Engineering Department has initiated his own program, which is cited in this report. During the past six months, in addition to 10 post-doctoral fellows or research associates (all Ph.D's), 31 graduate students worked on projects sponsored by this grant. In addition, 2 undergraduate students in the discipline of Chemistry worked on certain phases of projects sponsored by NASA. Six of the aforementioned 31 graduate students completed all requirements for the Ph.D. degree and nine others have completed all the requirements for the Master of Arts or Master of Science degree. These 15 graduate students are expected to receive their respective degrees at the end of May 1964. Also, during this period nine papers were published, four papers were accepted for publication and five were submitted to journals for publication. All of these resulted from work carried out under the grant and are summarized in an appendix to this report.

I. Solid State Physics

A. Paramagnetic Spin-Lattice Interactions

Dr. P. L. Donoho, Department of Physics

Work has been extended to include rare-earth materials which, in contrast to iron-group materials, exhibit surprising disagreement between theory and experiment. Theoretical work in this area is being started. Work in this general area, described in previous reports, has now been presented at meetings of the American Physical Society. Reference to these works are:

"Effect of Uniaxial Stress on the EPR Spectra of Nd^{3+} and U^{3+} Ions in CaF_2", by T. D. Black and P. L. Donoho, Bull. Am. Phys. Soc., 9, 37 (1964)

"Ultrasonic Paramagnetic Resonance of Uranium in CaF_2", by G. C. Wetzel, Jr. and P. L. Donoho, Bull. Am. Phys. Soc., 9, (1964)

B. Phonon-Phonon Interactions

Dr. P. L. Donoho, Department of Physics

A careful study has been made of the temperature dependence of microwave-ultrasonic attenuation in CaF_2. The results are in only partial agreement with existing theories, but point the way toward development of a better theory of the phonon-phonon interaction. A reference to previous work in this field indicates that some of the work has been presented at a meeting of the American Physical Society.

"Phonon-Phonon Interaction in CaF_2", by B. R. Breed, P. L. Donoho and B. Josephson, Jr., Bull. Am. Phys. Soc., 9 (1964)

C. Spin-Wave Phonon Interactions

Dr. P. L. Donoho, Department of Physics

The interactions of spin-waves in ferromagnetic and antiferromagnetic materials, particularly rare-earths, is being studied by microwave-ultrasonic techniques. Thin-film techniques are being perfected which will produce, hopefully, consistently reproducible results. At present, results cannot be interpreted meaningfully.

D. Superconductor Tunneling Interactions

Dr. P. L. Donoho, Department of Physics

The interaction of phonons with bound-pair electrons tunneling through an insulating junction between two superconductors is being studied by ultrasonic techniques. Most of the work at present is concentrated on producing good tunneling junctions.

E. Laser Research
Dr. T. A. Rabson, Department of Electrical Engineering

Results have been obtained indicating the polarization of each individual spike in the output of a Nd^{3+} glass laser rod, lasing at 1.06μ has a different polarization. A new experimental setup which will allow a complete measurement of polarization with a time resolution of $.1\mu$sec is being assembled. The effect of externally applied magnetic fields on the polarization of the spikes will also be studied with the new experimental arrangement.

This study should result in a better understanding of the lasing process and what gives rise to the spike nature of the output of most solid state optically pumped lasers. The effects of externally applied magnetic fields are of interest both as a possible internal modulation technique and as a means of gaining a better understanding of the interaction of the electromagnetic fields in a solid state laser with the paramagnetic ions which generate the laser action.

The same experiments as described above will also be carried out on a Nd^{3+} doped $CaWO_4$ crystals to see the effect of the different host matrix on the laser output.

F. Superconductivity of Niobium
Dr. W. V. Houston, Department of Physics

Work done the past 6 months has consisted of a continuation of the measurement of the losses in superconducting wires carrying 60 cycle heavy currents. It was shown that the losses could not be attributed to eddy currents because of the shape of the voltage vs. current traces on an oscilloscope. The losses were in general proportional to a relatively high power of the magnetic field at the surface of the wire. The superconducting state seemed to persist as long as the maximum field at the surface of the wire was as predicted by Silsbee's rule.

The work is being continued to investigate these matters in more detail.

G. Mechanics of Magnetic Ordering (Particularly Rare Earth Metals and Compounds)
Dr. G. Trammell, Department of Physics

Y. Kitano has investigated magnetic ordering in strong crystalline fields and has found the conditions under which the crystalline torques may prevent long range order at zero temperature while allowing such order in a finite temperature range. This work was reported on at the 1964 Spring meeting of the American Physical Society at Washington and is being written up for publication.

F. Specht has derived expressions for the non-isotropic indirect exchange couplings in the rare earth metals which arise from the non-spherical distributions of spin densities in the rare earth ions He finds non-isotropic corrections of the order of 50% in the case of the very non-spherical Cerium and Ytterbium and of the order of 10% for Holmium, near the middle of the series. This work is in its final stages and is being written up as a Ph.D thesis and for publication.

G. T. Trammell has shown (Physical Review, in press) in regards to the Bohm-Aharonov effect, that the vector potential term appearing in the expression for the Canonical momentum of a charged particle represents the interaction electromagnetic field momentum and is thus as "physical" as the proper momentum of the particle, which itself is partly electromagnetic in origin,

H. Nuclear Relaxation in Insulating Crystals
Dr. H. E. Rorschach, Jr. Department of Physics

This work is an investigation of the spin-lattice relaxation mechanism of nuclei in insulating crystals doped with various paramagnetic impurities important in laser crystals. The preliminary stages of this experiment involved the construction of a pulsed nuclear magnetic resonance spectrometer capable of supplying the large power required to saturate solids. This spectrometer was constructed by Dr. Morgan Waldrop and was used by him to investigate the temperature dependence of the relaxation times in CaF_2 doped with Uranium, Erbium, Europium, and Samarium. (Ph.D. Thesis "An Investigation of the Temperature Dependence of the Nuclear Spin-Lattice Relaxation Time of Fluorine Nuclei in Single Crystals of Calcium Fluoride Doped with Rare-Earth and Actinide Elements" (1963)). This work is being prepared for publication These experiments are continuing on the above crystals and other rare-earth doped crystals. Mr. Robert Burnett is now working on this project and should complete the requirements for a M. A. degree within the next year.

II. Physical Metallurgy

A. Electron Microscopy

Dr. W. Pfeiffer, Department of Mechanical Engineering

1. Experimental:

   a. Operating performance of the EM 200 electron microscope is still not completely satisfactory. Various repairs and modifications, especially on the electron gun and at various vacuum feed throughs have been necessary to make operation at 100 kv beam voltage possible. A new object stage, specifically designed for metallurgical work and a specimen chamber cooling device have been installed.

   b. Measurement of the image rotation at various magnifications and measurement of the angles between the image and diffraction pattern has been made. To calibrate the instrument as a tool for electron-diffraction studies a diffraction standard (Al-powder) has been employed.

   c. An investigation of the early stages of precipitation in Au-Co alloys has been initiated. Thin foils have been prepared. These foils exhibit small particles which are believed to be the ferromagnetic Co particles responsible for the high coercivity of these materials,

2. Theoretical:

   a. The previously-published displacement functions for edge dislocations in a semi-infinite region have been numerically computed and plotted for some parameters. The differences between these curves and those obtained from the functions for an infinite space are rather drastic in some cases.

   b. Computation of contrast curves has been extended to the case where the Burgers vector is oblique to the surface,

      A systematic study of the contrast phenomena of hexagonal dislocation loops, as described in earlier papers ((Phys. Stat. Sol. 2, 1727 (1962) and 3, 156 (1963)), has been undertaken. It turns out that for a given specimen and under certain diffraction conditions six different types of contrast formulation may be expected. Electronic computations pertaining to the four most interesting cases are currently in progress.

B. Plasticity Theory of Metal Single Crystals
Dr. W. Pfeiffer, Department of Mechanical Engineering

In A. Seeger's theory of the critical shear stress, τ_0, the activation volume, v, plays an important role. If τ_0/G (G = shear modulus) decreases linearly with increasing temperature, T ,and if only one thermally activated process is controlling the flow, then one can derive a differential equation for v(T) which is readily solved. It turns out that v increases slightly with T. The numerical value for Ni ($v = 4, 6 \cdot 10^{-19}$ cm^3) is in very good agreement with the value $4,9 \cdot 10^{-19}$ cm^3 obtained by M. Michelitsch (Z. Metallkunde 50, (1959)) from creep data.

C. The Effect of Controlled Solute Atom Addition and Temperature Upon Damping and Yield Phenomena in Magnesium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

Experimental studies are now complete upon the effect of a bias stress and tension and compression cycles upon damping behavior in high purity magnesium single crystals. Asymmetry of the first stress-strain loop after partial annealing at various bias stresses has been observed, The stress amplitude dependence of the energy loss appears to be independent of the bias stress. Holding the crystal at constant stress in the damping loop region, allowing some micro-creep to occur, causes a memory effect upon subsequently observed damping loops. The memory effect manifests itself as a kink in the stress-strain curve. It appears that it is possible different dislocations move during the loading and unloading portions of a closed unidirectional damping loop in magnesium.

The apparent elastic limit of magnesium at various stress levels in the damping loop regions is observed to vary rapidly with time. The elastic limit is defined as the first marked deviation from a linear stress-strain relation, which is within 10% of the expected isothermal modulus and is markedly below the macroscopic flow stress of the crystal. It can vary, for example, about 2 gm/mm^2 in 60 sec. at 400^{o}K. For high purity magnesium, the logarithm of the rate of change of the elastic limit is observed to decrease about linearly with reciprocal temperature between 400 to 300^{o}K.

From 300^{o}K to 130^{o}K the rate appears almost temperature independent. Similar studies on crystals doped with 0.1 atomic percent Al and Zn indicate, to date, that the rate of change of the elastic limit is faster, the more impure the crystal In fact, the rate for the zinc doped crystal is about 6 times as great as that for the Al doped crystal of similar impurity content. These rapid changes in the elastic limit occur in very short times (total times of about 300 secs.) and are believed to be related to very short-range migration of impurities to dislocation Preliminary results indicate the rate

of change of the elastic limit at constant temperature and time may be linear with the atomic percent Al in the crystal. The time dependence of the change in the elastic limit is being studied thoroughly as a function of concentration of impurities, prestrain and annealing history Attempts are being made to obtain the activation energy associated with this rapid pinning as well as to try to establish its correct interpretation.

The anelastic damping loops at constant stress amplitude decrease in size in at least two stages, one stage associated with the rapid pinning discussed above, the other occuring over a much longer period of time, namely about 160 mins. This slow change is not being studied thoroughly at present. It has been observed in the crystals noted above as well as a crystal containing 0.5 atomic percent Al. Mr. David Hartman will shortly write up the work as a Ph.D dissertation.

D. Microcreep in Single Crystals of Magnesium
Dr. J. M. Roberts, Department of Mechanical Engineering

Correlation between the microcreep data obtained in this laboratory with Seeger's theory for transient creep has been made. The latter theory should be valid only over small strain increments, a criterion which applies to the current data, Good agreement was found between values of the activation volume deduced from stress increment change tests (described in the last two Progress Reports) and those deduced from a single transient creep curve, the stress-strain curve at very low strain rate the the prediction of Seeger's theory. The temperature dependence of the stress necessary to produce a fixed microcreep rate in high purity magnesium single crystals has been checked. This stress appears to be temperature independent in the range 100° to 300°K. It should be noted however that for high-purity magnesium crystals unloading and reloading a crystal reproduces its ability to creep transiently, as if the crystal were unaware of the previous creep. It appears that it is essential to check the temperature dependence of the microcreep rate at constant τ^* for crystals doped with about 0.046% Al. This would be helpful, since the latter type crystals exhibit no anelastic recovery after unloading from a series of stress increment tests, yet the high purity magnesium crystals exhibit about 60% anelastic strain recovery after about 20 stress increment tests causing a total strain of about 10^{-4}. It should be noted that the present microcreep results go as high in strain rate as to overlap the work of Conrad and co-workers on macroscopic flow behavior by about one order of magnitude. The current results indicate that dislocation motion in high purity magnesium between 77° to 300°K is probably controlled by at least several different mechanisms. The latter is in agreement with the broad, low-frequency relaxation peaks which have been observed in high-purity magnesium in this laboratory. This work was reported at the Annual Meeting of the AIME in New York, 1964,

E. Dislocation Damping in Copper Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

No new experimental work has been done in this area within the past six months A general dislocation model is currently being investigated to explain the results obtained in this study. At present it does not appear that stress induced re-orientation of point defects is the likely origin of the damping behavior in copper. It now appears that an athermal dislocation point defect interaction in the temperature range studied can semi-qualitatively explain the results. Details concerning the variation of the internal stress and dislocation network size with prestrain seem important to understanding the experimental results. The latter are being investigated at present from data that is published in the literature. This work was reported at the Annual Meeting of the AIME in New York, 1964.

F. The Temperature Dependence of the Activation Volume, Work-Hardening Coefficient and Flow Stress of Cadmium Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

The most recent creep runs that were made are now almost completely analyzed. A clear idea of the temperature dependence of the activation volume should then be available. If the results check out satisfactorily, the data should be ready for preparation for publication.

G. Microcreep in Molybdenum Single Crystals
Dr. J. M. Roberts, Department of Mechanical Engineering

It has been concluded that measurement of the temperature dependence of the microcreep rate at constant effective stress should contribute substantially to understanding the slow behavior of any crystalline solid. The results on magnesium, to date, appear to be very complicated because of an overlap of various dislocation mechanisms in the temperature range investigated. Molybdenum exhibits a marked rise in flow stress with decreasing temperature at temperatures below room temperature and microcreep may only be controlled by one mechanism in this temperature range. Consequently, a detailed study of the effective stress and temperature dependence of microcreep in molybdenum single crystals is to be carried out The purpose of this is that it is hoped a meaningful value of the activation energy for microcreep at zero stress can be obtained. The specimen geometry and gripping arrangement has not been worked out Controlled orientation crystals will be used. One specimen is now prepared. Some modifications to the existing microcreep apparatus are currently being carried out. Preliminary tests are expected to be made in the near future.

H. Phonon-Dislocation Interactions

Drs. P. L. Donoho, Department of Physics, and J. M. Roberts and F. R. Brotzen, Department of Mechanical Engineering

The log decrement of LiF single crystals has been measured for longitudinal waves in the [111] orientation at room temperature and 4.2°K. The log decrement is independent of frequency between (600 to 1800) Mc at 4.2°K. The log decrement appears to go through a minimum at about 1200 Mc at room temperature. A resonant dislocation damping peak has not been found. The work of T. Suzuki et al, suggests, however, that the dislocation peak exists around 20 Mc. Further studies are required on annealed <110> and <100> oriented crystals before any conclusions can be drawn regarding the present results. In the latter experiments, a much larger shear stress will act upon dislocation and hence allow the dislocation effect to be investigated in detail. The results so far obtained are in complete agreement with the work of T. Suzuki et al, namely that the dislocations in LiF are overdamped and no natural dislocation resonant frequency peak in the kilomegacycle frequency range would be expected to be found. Various causes of modulation of the exponential decay of the acoustic wave have been investigated. Phonon-phonon relaxation mechanisms have also been investigated to account for some features of the results obtained.

I. An Electrical Resistivity Study of Deformed Molybdenum Single Crystals

Dr. F. R. Brotzen, Department of Mechanical Engineering

Single crystals of molybdenum were deformed in tension at 195°, 273°, 373° and 493°K. The influence of deformation temperature and intermediate annealing treatments at 473° and 422°K upon the electrical resistivity was investigated. All resistivity measurements were made at 4.2°K. The results indicate that:

a. Point defects are created during deformation at 195° and 273°K,

b. The rate with respect to strain at which these defects are produced is an inverse function of the deformation temperature,

c. Some or all of the point defects are mobile at 422°K and either coalesce or are lost at dislocations, and

d. This movement of the point defects does not affect the flow stress.

No definite conclusion was reached as yet on the dislocation model for the results, nor is the origin of the rapid rise of the activation volume above 300°K yet resolved. Further studies are in progress to check if the resistivity really does increase linearly with prestrain in molybdenum in this temperature range. An attempt to evaluate the relative magnitude of resistivity due to vacancies and dislocations will be made.

J. Ultrasonic Attenuation of LiF Single Crystals in the Temperature Range 2^{o} to $300^{o}K$ Both Before and After Prestraining and Co^{60} Gamma Irradiation

Drs. M. Yabe and J. M. Roberts, Department of Mechanical Engineering

A cryostat to carry out the irradiation and ultrasonic attenuation measurements has been designed. The system is now under construction and should be complete within a few weeks. In fact, almost all of the equipment is presently assembled. The manuscript mentioned in the previous report is now in almost final form. It will be submitted for publication in the near future. A theoretical study concerning phonon-phonon defect relaxation has been initiated.

K. Shear Fracture of Elastic Materials

Dr. J. Cl. DeBremaecker and L. Mansinha, Department of Geology

Since the last Semi-Annual Report, progress has been made in the theoretical investigation of fracture phenomenon, with particular reference to shear fractures. The behavior of shear fracture under hydrostatic pressure has been investigated by an extension of Yoffe's method. Shear fractures appear to exist at low hydrostatic pressure. Under high hydrostatic pressure the propagation of shear fracture is problematic. A paper titled "The Velocity of Shear Fracture Under Hydrostatic Pressure" was read at the 45th Annual Meeting of the American Geophysical Union, April 1964.

Work has also been completed on propagation of fractures along a welded bimaterial interface. The manuscript is under preparation and will be submitted for publication in the near future.

L. X-Ray and Resistivity Studies of Ti-V Alloys

Dr. F. R. Brotzen, Department of Mechanical Engineering

A detailed X-ray study of the rate of precipitation of the transition ω-phase in metastable β-phase titanium-base alloys of 15 to 25 nominal atomic weight percent vanadium has been completed. The results of this work indicate that the rate controlling factor in this precipitation process is an enhanced diffusion mechanism.

Additional work has indicated that the ω-phase precipitation rate can be strongly attenuated by very low temperature annealing ($<200^{o}C$), thus "stabilizing" the metastable β-phase. This effect, in conjunction with associated electrical resistivity measurements, has indicated the existence of a possible pre-precipitation phenomenon in these alloys. A more detailed investigation of this phenomenon is proposed for the next phase of this research program.

M. Kinetics of the Short-Range Ordering Reaction in Cu-Au
Dr. F. R. Brotzen, Department of Mechanical Engineering

The apparatus needed to carry out this study is still being assembled. The purpose and outline of the project was covered in the previous Report.

N. Superparamagnetic Particles
Dr. R. M. Asimow, Department of Mechanical Engineering

Work on superparamagnetism in the Au-Co system has been concluded and a paper based on this research submitted for publication. The results of this analysis show that it is possible by magnetic means to obtain quantitative information on the size, distribution, and shape of superparamagnetic precipitates.

O. Quenched-In Vacancies in Copper
Dr. R. M. Asimow, Department of Mechanical Engineering

Work on quenched-in resistivity in copper has been concluded and the results are described in the Master's thesis of Kou Chi Lin. The direct measurement of the free energy of formation of quenched-in vacancies in copper is proceeding. Preliminary measurements indicate that an emf of the right sign and magnitude is observed. Experiments are under way to determine whether reproducible results can be obtained. Most recent results indicate, however, that it may not be possible to obtain reproducible emf measurements at low cell impedance. The objectives of this project may change slightly because of this difficulty. This work is being done by Dr. Vir D. Anand, a Research Fellow.

P. Short-Range Order and Resistivity
Dr. R. M. Asimow, Department of Mechanical Engineering

A Ph.D thesis on the effects of deformation on the short range order in the platinum paladium system has been started. Initial experiments show that the resistance of these alloys does decrease with increasing plastic deformation.

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NOTE: The foregoing Projects A to K deal with fundamental studies related to the defect solid state, further knowledge of which is required for understanding the complex physical and mechanical properties of solids. Examples of the latter are, typically, fatigue, fracture and creep. The last five projects, L to P, center about research to develop a better understanding of some fundamental thermodynamic properties of metals and alloys. Projects A to P, dealing with lattice defects, transformations in solids, diffusion and precipitation, are all areas which must be more completely understood for the development of new engineering materials.

III. Chemistry of Solids

A. Order-Disorder Analysis of Lattice Systems

Dr. Z. W. Salsburg, Department of Chemistry

Monte Carlo calculations in a grand canonical ensemble are being used to study the thermodynamic behavior of "hard hexagon" lattice-gas models in which the hexagon centers are restricted to sites on the two-dimensional triangular lattice and the intermolecular potential is an infinite repulsion extending to $n^{\underline{th}}$ nearest neighbors. Some results have been obtained for n = 1, 2 and 3, and the following points have emerged to date:

1. For n = 1, calculations last Fall indicated a possible phase transition for an 81-site lattice containing 27 molecules at close packing ($\underset{\sim}{N}$ = 27). A 360-site lattice has now been studied ($\underset{\sim}{N}$ = 120), and the new results reinforce our earlier tentative conclusion that the apparent transition is not first-order but seems to be characterized by either a finite discontinuity or a singularity in the isothermal compressibility. A careful study of the compressibility in the "transition" region as a function of the number of lattice sites would be required to distinguish between these possibilities. This is not practical at present with the Rice computer and this study will be deferred until a larger memory is available or time can be obtained on another machine.

2. Results for n = 2 with a 360-site lattice ($\underset{\sim}{N}$ = 90) indicate a possible first-order phase transition near the apparent transition density for the hard-disc model. A very shallow "Van der Waals" loop is observed in the canonical ensemble chemical potential vs. density curve obtained by numerical differentiation of the grand ensemble Monte Carlo results. While the occurrence of such a loop is commonly interpreted as implying a first-order transition in the macroscopic limit, a careful study of size effects is again essential before any real confidence can be placed in this conclusion.

3. Limited results for n = 3 have shown the necessity for a change in the Monte Carlo sampling procedure. This case requires relatively large values of the chemical potential in order to reach the range of densities where phase transitions seem to occur for n = 1 and 2. Our present sampling method leads to effectively "locked" configurations at large chemical potentials and the Markov chain averages then converge too slowly for practical application. Several revised procedures are being considered which should improve the sampling.

B. Kinetic Measurements of the Rate of Oxidation of Nickel Foils at Elevated Temperatures
Dr. W. W. Akers, Department of Chemical Engineering

During the past six months, work has been completed on "The Kinetics Study of the Rate of Oxidation of Nickel at Elevated Temperatures". The results indicate that the oxidation proceeds by:

1. A nucleation process in which the rate increases rapidly with increased amounts of oxide,

2. Logarithmic rate step in which the rate decreases rapidly as the oxide later builds up, and

3. A parabolic region in which the rate is limited by a differential process.

C. Measurement of Emissivity of Nickel and Nickel-Oxide Surfaces at Elevated Temperatures
Dr. W. W. Akers, Department of Chemical Engineering

Work is being completed on the measurement of the emissivity of the nickel at elevated temperatures. The emissivity increases rapidly with the amount of oxide until approximately 50 micrograms per square centimeter have formed. Greater amounts of oxide have only a minor effect on the thermal emissivity. Work is continuing on this phase in order to obtain a more fundamental basis for thermal emission.

D. Mass-Spectrometric Studies of High Temperature Interactions Between Gases and Condensed Phases
Dr. J. L. Margrave, Department of Chemistry

The Bendix mass spectrometer and the magnetic mass spectrometer have been utilized for studies of a variety of high temperature gas-solid interactions. In addition, two microbalances are being utilized to provide information about vapor pressures from Knudson and Langmuir weight-loss measurements.

The species over the systems MnF_2, NiF_2, MnF_2-Mn and SeO_2 have been established mass spectrometrically and thermodynamic properties derived. Measurements on the vapor pressure of nickel are in progress. In addition, the stability of $AlF_2(g)$ has been determined by studies of the reaction between $MgF_2(s)$ and Al(l).

Vapor pressure work using the Knudsen effusion technique in conjunction with the vacuum microbalance has been divided into two phases. The low temperature phase (0-300°C) has concerned itself with the measurement of the vapor pressures of certain organic compounds in an attempt to correlate thermodynamic properties with

structural features. The compounds thus far studied have been 2,7-Dimethyl- Phenanthrene and 1'9-Domethyl-1,2-Benzanthracene. Enthalpies, free energies and entropies of evaporation are being evaluated from Second Law graphs and absolute pressures. By comparison of Δ S's for structurally related compounds one can determine the relationship between condensation coefficients and molecular geometry.

High temperature studies are to be done with the Ainsworth recording microbalance. This balance has been modified for high-vacuum operation and at this time, the balance is ready for operation with a fast pumping vacuum system which will reduce the pressure to the 10^{-6} Torr region. Studies of evaporation of inorganic solids at various high temperatures should be underway by the first or second week of June 1964.

Several runs with cesium as the molecular beam material were made on the open-faced velocity selector to see if a skewed velocity distribution was still obtained. Because of high detector noise levels, however, the results were inconclusive. The detector has been rewired and a new beam oven has been designed and installed. This oven, because of its exit slit being at the center of the selector disc, should eliminate many of the alignment problems previously encountered.

Some additional study has been made on the design of a concentric-ring velocity selector. It seems (as Bernstein has shown for slotted-disc selectors) that six concentric rings are necessary for elimination of all important side bands.

The change from surface-ionization detection to electron impact ionization with secondary electron multiplication is being studied since this change would put a more universal detector at our disposal.

E. Crystal Structures of Alkaline Earth Halides
Dr. R. L. Sass, Department of Chemistry

The crystal structure of $SrBr_2.H_2O$ has been determined by single crystal X-ray diffraction studies. The strontium atom is found to have a nearest-neighbor environment of seven bromine atoms at distances of from 3.13 Å to 3.38 Å and two water molecule oxygen atoms at 2.63 Å. This ninefold coordination is essentially the same as that found in the anhydrous barium halides.

Because of the smaller size of the strontium ion relative to barium, anhydrous $SrBr_2$ has a strontium coordination number of eight. The ninefold coordination is stabilized in the monohydrate because of the presence of the smaller oxygen atom.

F. Complex Ionic Solids
Dr. R. L. Sass, Department of Chemistry

The crystal structures of the carbanions ammonium tricyanomethide and pyridinium dicyanomethylide have been determined by single crystal X-ray diffraction studies. The unit cell constants of these compounds are:

	$NH_4C(CN)_3$	$C_8H_5N_3$
Space Group	$P2_1/C$	$P2_1/m$
a	9.055 Å	7.87 Å
b	3.87 Å	12.51 Å
c	17.32 Å	3.86 Å
β	104.6°	114.8°
z	4 molecules/cell	2 molecules/cell

The $C(CN)_3^-$ ion is singificantly nonplanar. The three C-C distances were measured to be 1.40 ± 0.01 Å and the three C-N distances were 1,15 ± 0.01 Å. The refined structure of the pyridinium dicyanomethylide molecule was planar in the pyridinium ring but nonplanar around the trigonally bonded carbon atom. The bond distances in this molecule are as follows: In the pyridinium ring the C-C distances are all 1.39 ± 0.01 Å, the C-N distance is 1.37 ± 0.01 Å. The pyridinium nitrogen to the trigonal carbon distance is 1.42 ± 0.01 Å; the trigonal carbon to the cyano carbon distance is 1.41 ± 0.01 Å and the C-N cyano distance is 1.13 ± 0.01 Å. The intramolecular bond angles are all normal.

G. Radiation Effects on Metallic Films and Surfaces of Solids
Dr. T. W. Leland, Department of Chemical Engineering

1. A paper on the effects of H_2 adsorption on the CdS films containing S^{35} has been completed and will be submitted for publication.

2. Studies of radiation induced impurity doping in cuprous oxide are continuing. An improved apparatus for measuring rates of dehydrogenation and dehydration of alcohols is under construction.

H. The Nature of Gaseous-Solid Interfaces
Dr. T. W. Leland, Department of Chemical Engineering

The initial series of experiments on the physical adsorption interaction of solid surfaces with high pressure gases has beem completed. The results are correlated very well by an improved 2-dimensional

equation of state derived from the 3-dimensional equation of state proposed by Eyring for dense fluids using a simple cell model. The results indicate a degree of ordering which occurs on the surface. A Ph.D dissertation has just been completed and accepted.

I. Chemisorption of Solids
Dr. H. A. Deans, Department of Chemical Engineering

Development of the experimental apparatus to measure chemisorption rates by perturbation chromatographic techniques is continuing.

J. Study of Hydrates
Dr. R. Kobayashi, Department of Chemical Engineering

Experimental and theoretical studies have been carried out on ternary systems forming hydrates. The systems chosen for the studies were methane-argon-water, argon-nitrogen-water and methane-nitrogen-water, and the experimental studies were carried out to a maximum preaaure of 1100 atmospheres.

The agreement of the experiment and theory for the initial hydrate formation conditions was found to be excellent for the first two systems with rather larger deviations for the selected argon-nitrogen-water mixture. The results of the last system are being recalculated using an intermolecular potential due to Kohara, which takes into account the non-spherical nature of the molecules.

The postulate that gas hydrates may occur in abundant quantities on some of the outer planets of our solar system has been made. Therefore, an improved understanding of their behavior will aid in the prediction of conditions for their existence on the planets.

K. Adsorption of Gases on Solids at Elevated Pressures
Dr. R. Kobayashi, Department of Chemical Engineering

General equations for obtaining component and total adsorption isotherms by a perturbation method have been developed recently by Gilmer and Kobayashi. The high pressure chromatographic equipment built by Gilmer is being modified for the detection of radioactive traced perturbations and for lower temperature service. The procedure developed by Gilmer, when completed, should provide a method for determining adsorption of multicomponent systems on solids with ease and accuracy.

Gas adsorption data are used in many areas of gas treatment for the space program. A novel application is the use of adsorbents for high speed pumping of adsorbable gases at low temperatures and pressures.

Signed: Franz R. Brotzen

Franz R. Brotzen

Dean of Engineering

May 31, 1964

APPENDIX

Papers Published, Manuscripts Submitted and Manuscripts Accepted in the Period Beginning November 15, 1963 and Ending May 15, 1964.

R. L. Sass, E. B. Brackett and T. E. Brackett, "The Crystal Structure of $PbCl_2$", J. Phys. Chem , 67, 2862 (1963)

R. L. Sass, E. B. Brackett and T. E. Brackett, "The Crystal Structure of $SrBr_2$", J. Phys. Chem., 61, 2862 (1963)

L. Mansinha, "Velocity of Shear Fracture", Bull. of Seis. Soc. of Am., 54, no 1, 369-376 (1964)

D. R. Marshall, S. Saito and R. Kobayshi, "Hydrates at High Pressure: Part I. Methane-Water, Argon-Water and Nitrogen-Water Systems", J. A.I.Ch.E., 10, 202 (1964)

R. M. Asimow, "Quenched-In Resistivity in Dilute Alloys", Phil. Mag., 9, 171 (1964)

R. M. Asimow, "Analysis of the Variation of the Diffusion Constant of Carbon in Austenite with Concentration", Trans. Met. Soc. A.I.M.E., 230, 611 (1964)

W. Pfeiffer, "Die Stufenversetzung im elastisch isotropen Halbraum", Zeit. für Naturforschung, 19a, 294 (1964)

P. L. Donoho and R. B. Hemphill, "Spin-Lattice Interaction in Ruby", Proc. VIIIth Int. Conf. on Low Temperature Physics, Butterworth, New York (1964)

P. L. Donoho, "Spin-Lattice Relaxation in Ruby", Phys Rev., 133, A1080, (1964)

C. Bugg, J. Lawson and R. L. Sass, "The Crystal Symmetry of Several Diazonium Salts", accepted for publication, Acta Cryst.

R. Desiderato and R. L. Sass, "The Crystal Structure of Ammonium Tricyanomethide", accepted for publication, Acta Cryst.

J. M. Roberts and D. E. Hartman, "The Temperature Dependence of the Microyield Points in Prestrained Magnesium Single Crystals", accepted for publication, Trans. A.I.M.E.

S. Saito, D. R. Marshall and R. Kobayashi, "Hydrates at High Pressures: Part II. Application of Statistical Mechanics and the Study of the Hydrates of Methane, Argon and Nitrogen", accepted for publication, J. A.I.Ch.E.

D. E. Hartman and J. R. Key, "An Integrator for X-Y Recorders", submitted for publication in Notes section of Rev. of Sc. Instr.

C. Bugg and R. L. Sass, "The Crystal Structure of Pyridinium Dicyanomethylide", submitted for publication, Acta Cryst.

M. Dyke and R. L. Sass, "The Crystal Structure of Strontium Bromide Monohydrate", submitted for publication, J. Am. Chem. Soc.

H. B. Gilmer and R. Kobayashi, "The Study of Gas-Solid Equilibrium at High Pressures by Gas Chromatography", submitted to A.I.Ch.E. J. November 15, 1963

S. Saito and R. Kobayashi, "Hydrates at High Pressures: Part III. Methane-Argon-Water, Methane-Nitrogen-Water and Argon-Nitrogen-Water Systems", submitted to J. A.I.Ch.E.